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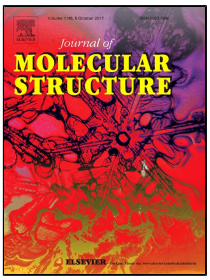

Distorted square-antiprism geometry of new zirconium (IV) Schiff base complexes: Synthesis, spectral characterization, crystal structure and investigation of biological properties

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Distorted square-antiprism geometry of new zirconium (IV) Schiff base complexes: Synthesis, spectral characterization, crystal structure and investigation of biological properties

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Abstract

A series of zirconium(IV) Schiff-base complexes formulated as $[Zr(L^x)_2]$ and $[Zr(L^{x\prime})_2]$ were synthesized by reaction of tetradentate salicylaldimine Schiff-base ligands with $[Zr(acac)_4]$ in methanol. These ligands are as follows: H_2L^x and $H_2L^{x\prime}$ (x=x′=1,2,3,4). The new complexes have been characterized using FT-IR, ^{1}H NMR, $^{13}C\{^1H\}$ NMR spectroscopic techniques, elemental analyses (CHN) and the crystal structure of $Zr(L^3)_2$, $Zr(L^{1\prime})_2$ and $Zr(L^{3\prime})_2$ were determined by X-ray crystallography. The crystal structure analysis revealed that the coordination environment of the metal in all complexes is eight-coordinate occupied by N_2O_2 sets of the coordinated ligands in distorted square-antiprism geometry. The *in vitro* biological screening effects of the synthesized compounds were tested against different microbial kinds and the zirconium(IV) complexes exhibit antimicrobial activity.

Keywords: N_2O_2 donor, Tetradentate Schiff-base ligands, Zirconium(IV) complexes, Distorted square-antiprism, Biological properties

Introduction

Schiff-base ligands are one of the most prevalent coordinating ligands in coordination chemistry. Schiff-base ligands such as salen (salicylaldiminatoethylenediamine) and salophen (salicylaldiminatophenylenediamine) and their metal complexes have a variety of biological, medicinal and analytical applications in addition to their important roles in catalysis and organic syntheses [1–4]. Metal complexes of Schiff-base ligands are sometimes more effective than their free ligands in catalytic activities [5–7]. Schiff-base complexes are also known as antifungal and anti-bacterial compounds [8, 9]. Therefore, experimental studies and also structural elucidation of these complexes is of great interest for chemists. In contrast to the considerable growth of literature on the chemistry of Schiff-base complexes of first row transition metals, the chemistry of the second and third row metal complexes such as zirconium is less well studied [10–14]. A high charge-to-size ratio ($Z^2/r = 22.22\ e^2\ m^{-10}$) of the zirconium(IV) ion gives it a marked tendency for higher coordination numbers including 7 and 8. Among the zirconium salts, $[Zr(acac)_4]$ is stable and low toxicity complex (LD_{50} {$[Zr(acac)_4]$ oral rat}=719 mg⁄kg) [15-17]. This compound can undergo partial or total exchange of monoanionic acetylacetonate (acac) with other suitable ligands to form various complexes. The continuing interest in eight-coordinate zirconium complexes is partly due to their potential application as components of coordination polymers [18–21] and also their coordination and structural chemistry [10–14].

According to the aforementioned points about the chemistry of zirconium Schiff base complexes, herein we report two types of zirconium(IV) Schiff-base complexes synthesized based on ligands derived from 2,2′-dimethyl-1,3-propanediamine and ligands derived from 4,5-dimethyl-1,2-phenylenediamine. These complexes were characterized using FT-IR, ^{1}H NMR, $^{13}C\{^1H\}$ NMR spectroscopic techniques, elemental analyses (CHN) and the crystal structures of $Zr(L^3)_2$, $Zr(L^{1'})_2$ and $Zr(L^{3'})_2$ were determined by X-ray crystallography. The *in vitro* biological screening effects of

the synthesized compounds were tested against different microbial kinds and the zirconium(IV) complexes exhibit antimicrobial activity.

Experimental

Chemicals and instrumentations

All chemicals are of reagent grade, used without more purification. ^{1}H and $^{13}C\{^{1}H\}$NMR spectra were recorded at ambient temperature with BRUKER AVANCE 400 MHz spectrometer using $CDCl_3$ as solvent. The chemical shift values (δ) are given in ppm. Infrared spectra were recorded from KBr pellets in the range from 4000 to 400 cm^{-1} using a Shimadzu FT-IR Prestige 21 spectrophotometer. Microanalyses (CHN) of the ligands and the complexes were carried out on a Leco CHNS elemental analyzer. For X-ray data collection light-yellow crystals were obtained by slow evaporation of a methanol solution of the respective complexes. X-ray data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Full spheres of reciprocal lattice were scanned by 0.3° steps in omega with a crystal–to–detector distance of 5 cm. Cell refinement and data reduction were performed with the help of the SAINT program [22]. Corrections for absorption were carried out with the multi-scan method and program SADABS [22]. The structures were solved with direct methods using SHELX2014/7 and structure refinement on F^2 was carried out with SHELX2014/7 program [23]. All non-hydrogen atoms were refined anisotropically. All calculations were done by PLATON [24].

Syntheses of Schiff-base ligands

The ligand H_2L^1 (3-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine was synthesized by adding 3-methoxy-salicylaldehyde (0.609 g, 4 mmol) to a solution of 4,5-dimethyl-1,2-phenylenediamine (0.272 g, 2 mmol) in ethanol (20 ml). After refluxing for 1.5 h the solution was left to evaporate slowly at room temperature. After 5 days, orange crystals of H_2L^1 were isolated.

The compound was characterized by using IR, ^{1}H NMR spectroscopy and elemental analyses (CHN). Other ligands were produced by this method. The X-ray structures of some of the ligands were reported in previous journal papers [25-27]

H_2L^1: (3-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine, Yield: 93 %, m.p.: 192 °C.

Anal. calcd. for $C_{24}H_{19}N_2O_4$ (%): C, 72.17; H, 4.79; N, 7.01. Found: C, 72.55; H, 4.68; N, 7.15.

IR (KBr, cm^{-1}): 1618 (C=N), 1574, 1465 (C=C), 1249 (C-O).

^{1}H NMR (400 MHz, $CDCl_3$): 13.38 (s, 2 H, O-H), 8.60 (s, 2 H, HC=N), 6.85 (t, ^3J = 7.85 Hz, 2 H, H_b), 6.95 (dd, ^3J = 8.0, ^4J = 1.2 Hz, 2 H, H_a), 6.99 (s, 2 H, H_d), 7.00 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2 H, H_c), 3.89 (s, 6 H, -OCH_3), 2.32 (s, 6 H, CH_3).

H_2L^2: (4-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine, Yield: 87 %, m.p.: 193 °C.

Anal. calcd. for $C_{24}H_{19}N_2O_4$ (%): C, 72.17; H, 4.79; N, 7.01. Found: C, 72.38; H, 4.87; N, 6.80.

IR (KBr, cm^{-1}): 1612 (C=N), 1591,1494 (C=C), 1292 (C-O).

^{1}H NMR (400 MHz, $CDCl_3$): 13.76 (s, 2 H, O-H), 8.53 (s, 2 H, HC=N), 6.46 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 2 H, H_b), 6.55 (d, ^4J = 2.4 Hz, 2 H, H_a), 7.00 (s, 2 H, H_d), 7.24 (d, ^3J = 8.6 Hz, 2 H, H_c), 3.83 (s, 6 H, -OCH_3), 2.31 (s, 6 H, CH_3).

H_2L^3: (5-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine, Yield: 91 %, m.p.: 135 °C.

Anal. calcd. for $C_{24}H_{19}N_2O_4$ (%): C, 72.17; H, 4.79; N, 7.01. Found: C, 72.42; H, 4.88; N, 6.93.

IR (KBr, cm^{-1}): 1618 (C=N), 1575,1487 (C=C), 1271 (C-O).

^{1}H NMR (400 MHz, $CDCl_3$): 12.74 (s, 2 H, O-H), 8.60 (s, 2 H, HC=N), 7.04 (s, 2 H, H_c), 6.99 (s, 2 H, H_d), 6.98 (d, ^3J = 8.0 Hz, 2 H, H_a), 6.88 (d, ^3J = 8.0 Hz, 2 H, H_b), 3.80 (s, 6 H, -OCH_3), 2.34 (s, 6 H, CH_3).

H_2L^4: (6-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine, Yield: 84 %, m.p.: 201 °C.

Anal. calcd. for $C_{24}H_{19}N_2O_4$ (%): C, 72.17; H, 4.79; N, 7.01. Found: C, 72.53; H, 4.87; N, 6.91.

IR (KBr, cm^{-1}): 1612 (C=N), 1595,1462 (C=C), 1249 (C-O).

^{1}H NMR (400 MHz, $CDCl_3$): 14.14 (s, 2 H, O-H), 9.11 (s, 2 H, HC=N), 7.22 (t, ^3J = 8.0 Hz, 2 H, H_b), 7.03 (s, 2 H, H_d), 6.63 (d, ^3J = 8.0 Hz, 2 H, H_c), 6.34 (d, ^3J = 8.0 Hz, 2 H, H_a), 3.86 (s, 6 H, -OCH_3), 2.33 (s, 6 H, CH_3).

The ligand $H_2L^{1'}$ (3-methoxysalicylidene)-2,2-dimethyl-1,3-propandiamine was synthesized by adding 3-methoxy-salicylaldehyde (0.609 g, 4 mmol) to a solution of 2,2-dimethyl-1,3-propanediamine (0.204 g, 2 mmol) in ethanol (20 ml). After refluxing for 2 h the solution was left to evaporate slowly at room temperature. After 7 days, yellow crystals of $H_2L^{1'}$ were isolated. The compound was characterized by using IR, ^{1}H NMR spectroscopy and elemental analyses (CHN). Other ligands were produced by this method. The X-ray structures of some of the ligands were reported in previous journal papers [28-30].

$H_2L^{1'}$: (3-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine, Yield: 89 %, m.p.: 102 °C.

Anal. calcd. for $C_{21}H_{26}N_2O_4$ (%): C, 68.09; H, 7.07; N, 7.56. Found: C, 68.49; H, 7.19; N, 7.37.

IR (KBr, cm^{-1}): 1627 (C=N), 1475 (C=C), 1253 (C-O).

^{1}H NMR (400 MHz, $CDCl_3$): 14.12 (broad s, 2 H, O-H), 8.20 (s, 2 H, HC=N), 7.15 (d, ^3J = 8.5 Hz, 2 H, H_a), 6.47 (d, ^4J = 2.4 Hz, 2 H, H_c), 6.44 (dd, ^3J = 8.5 Hz, ^4J = 2.4 Hz, 2 H, H_b), 3.86 (s, 6 H, -OCH_3), 3.45 (s, 4 H, H_d), 1.10 (s, 6 H, CH_3).

$H_2L^{2'}$: (4-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine, Yield: 78 %, m.p.: 103 °C.

Anal. calcd. for $C_{21}H_{26}N_2O_4$ (%): C, 68.09; H, 7.07; N, 7.56. Found: C, 67.88; H, 7.19; N, 7.42.

IR (KBr, cm^{-1}): 1627 (C=N), 1442 (C=C), 1222 (C-O).

^{1}H NMR (400 MHz; $CDCl_3$): 13.28 (broad s, 2 H, O-H), 8.46 (s, 2 H, HC=N), 7.61 (d, ^3J = 8.0 Hz, 2 H, H_c), 6.43 (dd, ^3J = 8.0 Hz, ^4J = 2.4, 2 H, H_b), 6.37 (d, ^4J = 2.4 Hz, 2 H, H_c), 3.74 (s, 6 H, -OCH_3), 3.31 (s, 4 H, H_d), 0.97 (s, 6 H, CH_3).

$H_2L^{3'}$: (5-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine, Yield: 83 %, m.p.: 89 °C.

Anal. calcd. for $C_{21}H_{26}N_2O_4$ (%): C, 68.09; H, 7.07; N, 7.56. Found: C, 68.33; H, 6.95; N, 7.65.

IR (KBr, cm^{-1}): 1637 (C=N), 1494 (C=C), 1271 (C-O).

^1H NMR (400 MHz; $CDCl_3$): 13.03 (broad s, 2 H, O-H), 8.28 (s, 2 H, HC=N), 6.94 (d, ^3J = 8.8 Hz, 2 H, H_a), 6.92 (dd, ^3J = 8.8 Hz, ^4J = 2.7, 2 H, H_b), 6.77 (d, ^4J = 2.7 Hz, 2 H, H_c), 3.77 (s, 6 H, -OCH_3), 3.48 (s, 4 H, H_d), 1.07 (s, 6 H, CH_3).

$H_2L^{4'}$: (6-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine, Yield: 75 %, m.p.: 116 °C.

Anal. calcd. for $C_{21}H_{26}N_2O_4$ (%): C, 68.09; H, 7.07; N, 7.56. Found: C, 68.34; H, 7.01; N, 7.35.

IR (KBr, cm^{-1}): 1624 (C=N), 1467 (C=C), 1249 (C-O).

^1H NMR (400 MHz; $CDCl_3$): 14.68 (broad s, 2 H, O-H), 8.76 (s, 2 H, HC=N), 7.22 (t , ^3J = 8.2 Hz, 2 H, Hb), 6.54 (d, ^3J = 8.2 Hz, 2 H, H_a), 6.27 (d, ^3J = 8.2 Hz, 2 H, H_c), 3.81 (s, 6 H, -OCH_3), 3.47 (s, 4 H, H_d), 1.06 (s, 6 H, CH_3).

Syntheses of zirconium(IV) Schiff-base complexes

$Zr(L^1)_2$: [bis(3-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine] zirconium, Yield: 89%. The Schiff-base bis(3-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine (0.809 g, 2 mmol) was dissolved in freshly distilled methanol (30 mL). To this yellow solution was added [$Zr(acac)_4$] (0.488 g, 1 mmol) in one portion. The reaction mixture was then stirred and maintained at the reflux temperature for 4 h. After filtration of the suspension with a cannula, the filtrate was concentrated and a light yellow crystalline solid appeared over a period of several days. The solid was washed twice with Et_2O and dried *in vacuo*. Yellow crystals suitable for X-ray analysis were grown from a methanol solution of complex $Zr(L^1)_2$. This complex was characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analyses (CHN).

Anal. calcd. for $C_{48}H_{44}N_4O_8Zr$ (%): C, 64.34; H, 4.95; N, 6.25. Found: C, 64.54; H, 5.05; N, 5.97.

IR (KBr, cm^{-1}): 1618, 1593 (C=N), 1550, 1469 (C=C), 1313 (C-O), 559 (Zr-O), 416 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.88 (s, 2 H, $H_{i'}$-C=N), 8.21 (s, 2 H, H_i-C=N), 7.80 (s, 2 H, $H_{d'}$), 7.04 (dd, ^{3}J = 8 Hz, ^{4}J = 1.6 Hz, 2 H, $H_{c'}$), 6.85 (dd, ^{3}J = 8 Hz, ^{4}J = 1.6 Hz, 2 H, H_c), 6.60 (t, J = 7.6 Hz, 2 H, $H_{b'}$), 6.54 (t, J = 7.6 Hz, 2 H, H_b), 6.49 (dd, ^{3}J = 8 Hz, ^{4}J = 1.6 Hz, 2 H, $H_{a'}$), 6.39 (s, 2 H, H_d), 6.37 (dd, ^{3}J = 8 Hz, ^{4}J = 1.6 Hz, 2 H, H_a), 3.49 (s, 6 H, -$OCH_{3(o')}$), 3.43 (s, 6 H, -$OCH_{3(o)}$), 2.42 (s, 6 H, -$CH_{3(m')}$), 2.14 (s, 6 H, -$CH_{3(m)}$).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 293 K): δ 161.32, 159.66, 156.67, 154.62, 150.88, 149.72, 143.32, 143.25, 135.69, 134.84, 125.24, 124.03, 122.88, 121.72, 119.15, 117.66, 115.89, 115.18, 112.52, 111.64, 54.47, 54.38, 20.07, 19.63.

$Zr(L^2)_2$: [bis(4-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine] zirconium, Yield: 81%.

Anal. calcd. for $C_{48}H_{44}N_4O_8Zr$ (%): C, 64.34; H, 4.95; N, 6.25. Found: C, 64.52; H, 5.07; N, 6.03.

IR (KBr, cm^{-1}): 1608, 1593 (C=N), 1589, 1438 (C=C), 1311 (C-O), 536 (Zr-O), 433 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.67 (s, 2 H, $H_{i'}$-C=N), 8.14 (s, 2 H, H_i-C=N), 7.62 (s, 2 H, $H_{d'}$), 7.21 (d, ^{3}J = 8.8 Hz, 2 H, $H_{c'}$), 7.05 (d, ^{3}J = 8.4 Hz, 2 H, H_c), 6.52 (s, 2 H, H_d), 6.23 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.4 Hz, 2 H, $H_{b'}$), 6.20 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.4 Hz, 2 H, H_b), 5.72 (d, ^{4}J = 2.4 Hz, 2 H, $H_{a'}$), 5.44 (d, ^{4}J = 2.4 Hz, 2 H, H_a), 3.55 (s, 6 H, -$OCH_{3(o')}$), 3.52 (s, 6 H, -$OCH_{3(o)}$), 2.39 (s, 6 H, -$CH_{3(m')}$), 2.13 (s, 6 H, -$CH_{3(m)}$).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 293 K): δ 169.59, 166.75, 164.99, 164.80, 159.09, 158.135, 143.95, 143.73, 134.51, 134.41, 133.68, 133.43, 118.37, 117.87, 116.90, 115.99, 107.16, 106.90, 103.75, 102.41, 55.06, 54.72, 19.98, 19.36.

$Zr(L^3)_2$: [bis(5-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine] zirconium, Yield: 86%.

The title compound was synthesized like the previous method. Dark red single crystals of the title compound, that was suitable for X-ray structure analysis, were obtained by the slow evaporation at RT of a solution in methanol during a period of the days.

Anal. calcd. for $C_{48}H_{44}N_4O_8Zr$ (%): C, 64.34; H, 4.95; N, 6.25. Found: C, 64.47; H, 5.02; N, 6.34.

IR (KBr, cm^{-1}): 1620, 1589 (C=N), 1539, 1463 (C=C), 1301 (C-O), 518 (Zr-O), 448 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.67 (s, 2 H, $H_{i'}$-C=N), 8.20 (s, 2 H, H_i-C=N), 7.66 (s, 2 H, $H_{d'}$), 6.77 (d, ^4J = 3.2 Hz, 2 H, $H_{c'}$), 6.62 (s, 2 H, H_d), 6.60 (d, ^4J = 3.2 Hz, 2 H, H_c), 6.55 (dd, ^3J = 9.2 Hz, ^4J = 3.2 Hz, 2 H, $H_{b'}$), 6.52 (dd, ^3J = 9.2 Hz, ^4J = 3.2 Hz, 2 H, H_b), 6.10 (d, ^3J = 9.2, 2 H, $H_{a'}$), 5.77 (d, ^3J = 9.2, 2 H, H_a), 3.76 (s, 6 H, -$OCH_{3(o')}$), 3.75 (s, 6 H, -$OCH_{3(o)}$), 2.43 (s, 6 H, -$CH_{3(m')}$), 2.17 (s, 6 H, -$CH_{3(m)}$).

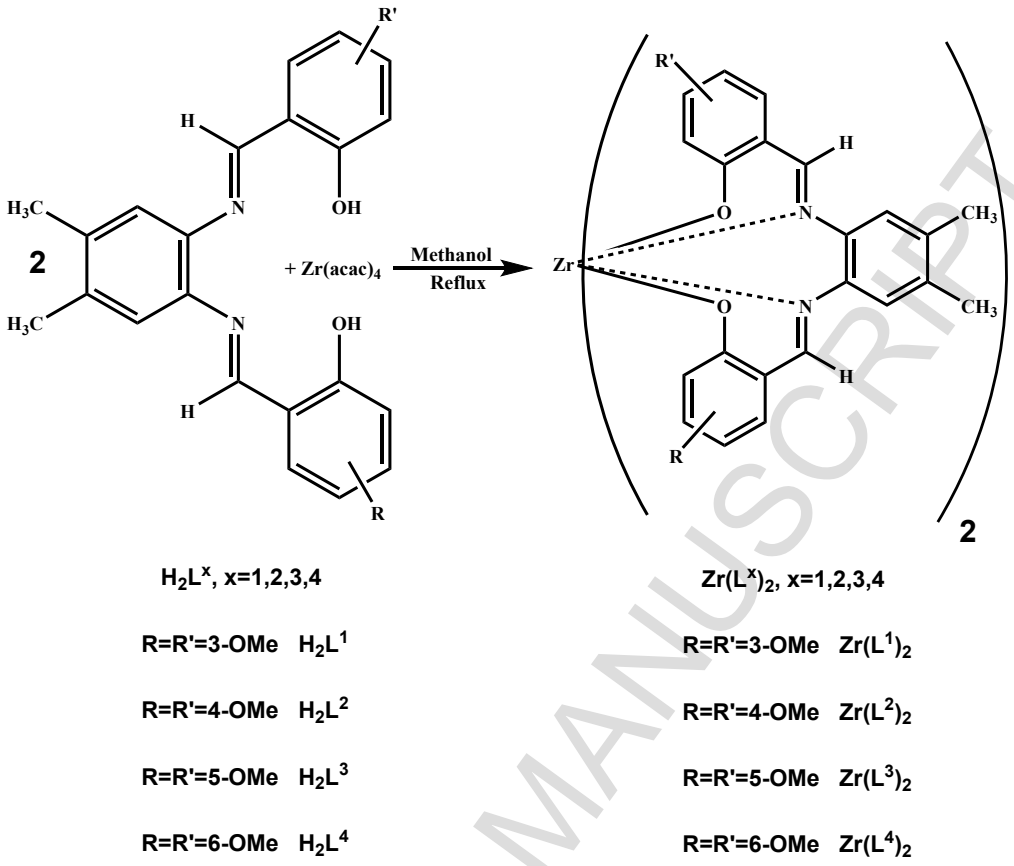
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 293 K): δ 165.09, 164.02, 162.66, 159.79, 158.90, 155.27, 154.99, 149.96, 143.65, 143.55, 135.85, 135.14, 122.95, 122.38, 121.10, 120.35, 118.73, 118.34, 113.60, 113.03, 56.19, 55.86, 19.97, 19.55.

$Zr(L^4)_2$: [bis(6-methoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamine] zirconium, Yield: 78%. Anal. calcd. for $C_{48}H_{44}N_4O_8Zr$ (%): C, 64.34; H, 4.95; N, 6.25. Found: C, 64.53; H, 5.12; N, 6.02.

IR (KBr, cm^{-1}): 1610, 1581 (C=N), 1544, 1460 (C=C), 1319 (C-O), 569 (Zr-O), 416 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 9.26 (s, 2 H, $H_{i'}$-C=N), 8.79 (s, 2 H, H_i-C=N), 7.64 (s, 2 H, $H_{d'}$), 6.80 (t, ^3J = 8.4 Hz, 2 H, $H_{b'}$), 6.75 (t, ^3J = 8.4 Hz, 2 H, H_b), 6.55 (s, 2 H, H_d), 6.01 (d, ^3J = 8 Hz, 2 H, $H_{a'}$), 6.94 (d, ^3J = 8 Hz, 2 H, H_a), 5.87 (d, ^3J = 8.4 Hz, 2 H, $H_{c'}$), 5.50 (d, ^3J = 8.4 Hz, 2 H, H_c), 3.90 (s, 6 H, -$OCH_{3(o')}$), 3.83 (s, 6 H, -$OCH_{3(o)}$), 2.41 (s, 6 H, -$CH_{3(m')}$), 2.14 (s, 6 H, -$CH_{3(m)}$).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 293 K): δ 167.54, 165.15, 160.28, 160.19, 155.20, 154.82, 144.41, 144.33, 135.20, 134.64, 133.25, 132.92, 118.96, 118.51, 114.96, 114.35, 113.30, 112.32, 96.96, 96.17, 55.80, 55.61, 19.89, 19.46. (For synthetic method to the formation of $Zr(L^x)_2$ complexes see Scheme 1)



Scheme 1. Synthetic pathway to $Zr(L^x)_2$ complexes

$Zr(L^{1'})_2$:[bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine] zirconium(IV),Yield: 82%. By adding bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine (0.741 g, 2 mmol) to a solution of $Zr(acac)_4$ (0.488 g, 1 mmol) in methanol (20 ml) the title compound was synthesized. The mixture was refluxed with stirring for 5 hours. Then the resultant light yellow solution was filtered. Colorless single crystals of the title compound, that was suitable for *X*-ray structure analysis, were obtained by the slow evaporation at RT of a solution in methanol during several days. This complex was characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, IR spectroscopy, elemental analyses (CHN) and its solid state structure was determined using single crystal X-ray diffraction. Anal. calcd. for $C_{42}H_{50}N_4O_8Zr$ (%): C, 60.77; H, 6.07; N, 6.75. Found: C, 60.54; H, 6.19; N, 6.54. IR (KBr, cm^{-1}): 1629, 1599 (C=N), 1558, 1456 (C=C), 1315 (C-O), 555 (Zr-O), 426 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.08 (s, 4 H, HC=N), 6.61 (d, ^3J = 7.6 Hz, 4 H, H_c), 6.34 (t, ^3J = 7.6 Hz, 4 H, H_b), 6.28 (d, ^3J = 7.6 Hz, 4 H, H_a), 5.75 (d, J = 10.8 Hz, 4 H, $H_{d'}$), 3.53 (s, 12 H, -OCH_3), 2.92 (d, J = 10.8 Hz, 4 H, H_d), 1.31 (s, 12 H, -CH_3).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ 165.31, 154.53, 149.83, 122.52, 121.99, 114.63, 111.93, 68.42, 54.32, 37.47, 25.30.

$Zr(L^{2'})_2$:[bis (4-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine] zirconium(IV),Yield: 77%.

Anal. calcd. for $C_{42}H_{50}N_4O_8Zr$ (%): C, 60.77; H, 6.07; N, 6.75. Found: C, 60.89; H, 6.12; N, 6.63.

IR (KBr, cm^{-1}): 1600, 1612 (C=N), 1523, 1442 (C=C), 1311 (C-O), 536 (Zr-O), 464 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 292.6 K): δ 8.17 (s, 4 H, HC=N), 7.12 (d, ^3J = 8.8 Hz, 4 H, H_c), 6.44 (d, ^4J = 2.4 Hz, 4 H, H_a), 6.41 (dd, ^3J = 8.8 Hz, ^4J =2.4 Hz, 4 H, H_b), 5.08 (d, J = 11.0 Hz, 4 H, $H_{d'}$), 3.83 (s, 12 H, -OCH_3), 2.98 (d, J = 11.0 Hz, 4 H, H_d), 1.07 (s, 12 H, -CH_3).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 293 K): δ 165.77, 164.67, 134.38, 132.68, 106.40, 103.06, 101.22, 66.53, 55.38, 36.25, 24.89.

$Zr(L^{3'})_2$:[bis (5-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine] zirconium(IV),Yield: 81%.

The yellow solid complex was prepared in a similar manner described above. Light yellow single crystals of the title compound, suitable for *X*-ray structure analysis, were obtained by slow evaporation at RT of a solution in methanol during several days.

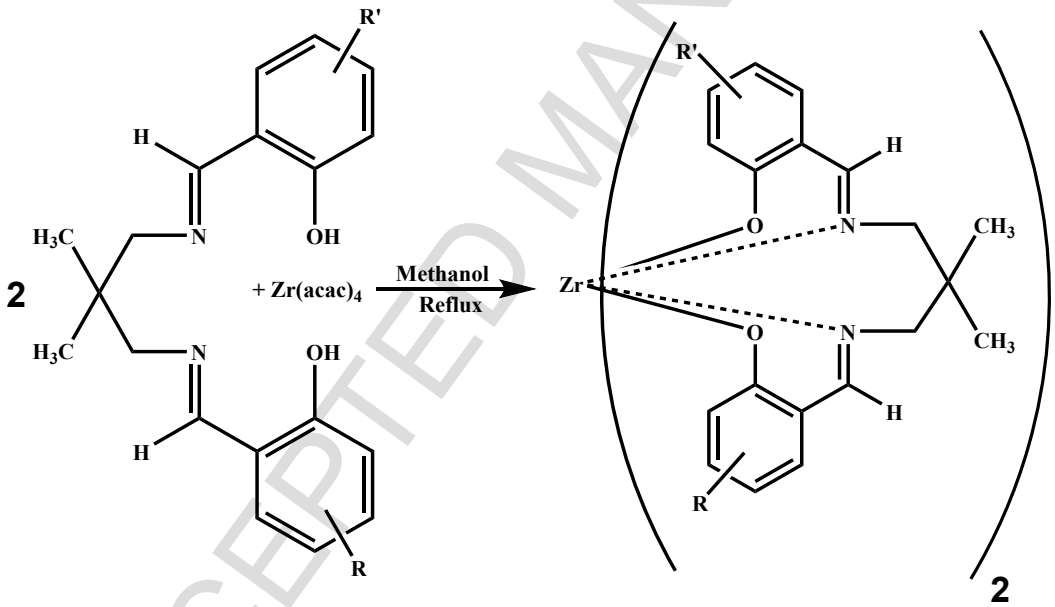
Anal. calcd. for $C_{42}H_{50}N_4O_8Zr$ (%): C, 60.77; H, 6.07; N, 6.75. Found: C, 60.82; H, 6.15; N, 6.84.

IR (KBr, cm^{-1}): 1633, 1604 (C=N), 1556, 1479 (C=C), 1298 (C-O), 518 (Zr-O), 441 (Zr-N).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.02 (s, 4 H, HC=N), 6.53 (d, ^4J = 3.2 Hz, 4 H, H_c), 6.47 (dd, ^3J = 8.8 Hz, ^4J = 3.2 Hz, 4 H, H_b), 6.06 (d, ^3J = 8.8 Hz, 4 H, H_a), 5.19 (d, J = 11.2 Hz, 4 H, $H_{d'}$), 3.66 (s, 12 H, -OCH_3), 3.00 (d, J = 11.2 Hz, 4 H, H_d), 1.26 (s, 12 H, -CH_3).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 293.2 K): δ 164.97, 158.60, 149.74, 121.33, 120.74, 120.05, 114.38, 69.40, 56.25, 36.96, 25.59.

$Zr(L^{4'})_2$:[bis (6-methoxysalicylidene)-2,2-dimethyl-1,3-propanediamine] zirconium(IV),Yield: 72%. Anal. calcd. for $C_{42}H_{50}N_4O_8Zr$ (%): C, 60.77; H, 6.07; N, 6.75. Found: C, 60.52; H, 6.12; N, 6.88. IR (KBr, cm^{-1}): 1618, 1600 (C=N), 1560, 1460 (C=C), 1313 (C-O), 542 (Zr-O), 424 (Zr-N). ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 8.50 (s, 4 H, HC=N), 6.75 (t, ^3J = 8.2 Hz, 4 H, H_b), 5.90 (d, ^3J = 8.2 Hz, 4 H, H_c), 5.84 (d, ^3J = 8.2 Hz, 4 H, H_a), 5.18 (d, J = 11.0 Hz, 4 H, $H_{d'}$), 3.75 (s, 12 H, -OCH_3), 2.98 (d, J = 11.0 Hz, 4 H, H_d), 1.25 (s, 12 H, -CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 294 K): δ 163.89, 160.12, 133.69, 132.23, 112.69, 110.75, 97.39, 69.64, 55.69, 36.70, 25.31. (For synthetic method to the formation of $Zr(L^{x'})_2$ complexes see Scheme 2)



$H_2L^{x'}$, x'=1,2,3,4

R=R'=3-OMe $H_2L^{1'}$

R=R'=4-OMe $H_2L^{2'}$

R=R'=5-OMe $H_2L^{3'}$

R=R'=6-OMe $H_2L^{4'}$

$Zr(L^{x'})_2$, x'=1,2,3,4

R=R'=3-OMe $Zr(L^{1'})_2$

R=R'=4-OMe $Zr(L^{2'})_2$

R=R'=5-OMe $Zr(L^{3'})_2$

R=R'=6-OMe $Zr(L^{4'})_2$

Scheme 2. Synthetic pathway to $Zr(L^{x'})_2$ complexes

In vitro Antibacterial activity

The antibacterial activities of the Schiff-base ligands and their zirconium(IV) complexes were tested against the bacterial species *Escherichia coli* ATCC 25922 (gram negative bacteria) and *Staphylococcus aureus* ATCC 25923 (gram positive bacteria) by the disc diffusion method. The primary screening was performed using agar well diffusion at fixed concentrations of 10 mg/ml by dissolving in 10% DMSO. The experiments were performed in triplicates. The MIC of the chemically synthesized compounds were tested against bacterial strains through a broth dilutions method. The test concentrations of chemically synthesized compounds were made from 128 to 0.25 mg/ml in the sterile.

Results and Discussion

Syntheses

The Schiff-base ligands were synthesized from 4,5-dimethyl-1,2-phenylenediamine and 2,2′-dimethyl-1,3-propanediamine, respectively, in a Schiff-base condensation reaction with methoxysalicylaldehyde, in ethanol. A one-pot reaction of $Zr(acac)_4$ and the related tetradentate Schiff-base ligands H_2L^x and $H_2L^{x\prime}$ (x=x′=1,2,3,4), in refluxing methanol, afforded the neutral zirconium(IV) complexes. Both ligands and the related complexes were obtained in high yields and are stable in the solid state and in solution. The complexes are light-yellow solids and could be crystallized out from methanol.

3.2. Spectroscopic characterization

FT-IR Spectra

The information about the stretching frequencies of the C=N and C-O bonds of the ligands and their corresponding Zr(IV) complexes are summarized in Table 1. The strong bands around 1612-

1637 cm^{-1} in the FT-IR spectra of ligands are attributed to the azomethine stretching band which are red shifted to 1581-1633 cm^{-1} upon coordination to Zr(IV) ion. While the C-O stretching band of the ligands shift from 1222-1292 cm^{-1} to 1298-1315 cm^{-1} upon coordination to Zr(IV) ion. These observations are in accordance with the data obtained for the C=N and C-O bonds lengths by X-ray crystallography in which the C=N bond is weakened by coordination to Zr(IV). In contrast, the C-O bond is strengthened upon coordination to Zr(IV) [31-37]. This is extremely supported by the disappearance of the broad, (O-H) band in the (3300-3150 cm^{-1}) region in the complexes. The medium sharp bands at 518-569 and 416-464 cm^{-1} can be related to Zr-O and Zr-N bonds, respectively [33, 38, 39].

Table 1. IR spectral data of the ligands and their corresponding Zr(IV) complexes

Compound	υ(C=C)	υ(C-O)	υ(C=N)	υ(Zr-O)	υ(Zr-N)
H_2L^1	1574, 1465	1249	1618	-	-
$Zr(L^1)_2$	1550, 1469	1313	1618, 1593	559	416
H_2L^2	1591, 1494	1292	1612	-	-
$Zr(L^2)_2$	1589, 1438	1311	1608, 1589	536	433
H_2L^3	1575, 1487	1271	1618	-	-
$Zr(L^3)_2$	1539, 1463	1301	1620, 1589	518	448
H_2L^4	1595,1462	1249	1612	-	-
$Zr(L^4)_2$	1544, 1460	1319	1610, 1581	569	416
$H_2L^{1'}$	1525,1463	1253	1612	-	-
$Zr(L^{1'})_2$	1558, 1456	1315	1629, 1599	555	426
$H_2L^{2'}$	1512,1442	1222	1627	-	-
$Zr(L^{2'})_2$	1523, 1442	1311	1612, 1600	536	464
$H_2L^{3'}$	1494,1467	1271	1637	-	-
$Zr(L^{3'})_2$	1556, 1479	1298	1633, 1604	518	441
$H_2L^{4'}$	1577,1467	1249	1624	-	-
$Zr(L^{4'})_2$	1560,1460	1313	1618, 1600	542	424

^1H NMR, $^{13}C\{^1H\}$ NMR Spectra

The ^1H NMR spectra of the Schiff-base ligands and zirconium(IV) complexes were taken in $CDCl_3$ (400 MHz, 298 K). In the ^1H NMR spectrum of the $Zr(L^1)_2$ complex (Fig. 1), the signals at δ = 8.88

and δ = 8.21 ppm are assigned to the $H_{i'}$-C=N- and H_i-C=N- proton of azomethine, respectively. Appearance of two ^{1}H NMR peaks for azomethine protons present in the $Zr(L^1)_2$ complex are indicative of the magnetically non-equivalence environment of these protons. The ^{1}H NMR spectra of the ligands, show the disappearing of phenolic proton signal and downfield shift of the azomethine H, confirming the coordination of the phenolic oxygen and azomethine nitrogen to Zr atom. The aromatic protons of the $Zr(L^1)_2$ complex appear in the range of δ = 6.36–7.80 ppm. H_a and $H_{a'}$ signals observed at 6.37 and 6.49 ppm as a doublet of doublet due to coupling with H_b, H_c and $H_{b'}$, $H_{c'}$ [^3J = 8.0 Hz and ^4J = 1.6 Hz] respectively. H_b and $H_{b'}$ signals appeared at 6.54 and 6.60 ppm as a triplet due to the couplings with H_a, H_c and $H_{a'}$, $H_{c'}$, respectively. The signals due to $H_{d'}$ and $H_{c'}$ obsereved as singlet and doublet of doublet [^3J = 8.0 Hz and ^4J = 1.6 Hz] at 7.80 and 7.04 ppm, respectively. H_c signal appeared at 6.85 ppm as a doublet of doublet due to the coupling with H_b [^3J = 8.0 Hz] and H_a [^4J = 1.6 Hz]. The H_d is observed as a singlet at δ= 6.39 ppm. The $–CH_{3(o')}$ and $–CH_{3(o)}$ are observed as a singlet at δ = 3.49 and δ = 3.43 ppm, respectively. The $–CH_{3(m')}$ and $–CH_{3(m)}$ are observed as a singlet at δ = 2.42 and δ = 2.14 ppm, respectively.

In the ^{1}H NMR spectrum of the $Zr(L^{1\prime})_2$ complex (Fig. 3), the signal δ = 8.08 ppm is assigned to the H_i-C=N- proton of azomethine. The aromatic protons of the $Zr(L^{1\prime})_2$ complex appear in the range of δ = 6.27–6.62 ppm. H_c signal appeared at 6.61 ppm as a doublet due to the coupling with H_b [^3J = 7.6 Hz]. H_b signal appeared at 6.34 ppm as a triplet due to the couplings with H_a and H_c. H_a signal appeared at 6.28 ppm as a doublet of doublet due to the coupling with H_b [^3J = 7.6 Hz]. $H_{d'}$ and H_d signals observed at 5.75 and 2.92 ppm as a doublet due to coupling with H_d and $H_{d'}$, respectively. A singlet at δ= 3.53 ppm is assigned to the $–OCH_3$ protons and the $–CH_3$ is observed as a singlet at δ = 1.31 ppm.

The $^{13}C\{^1H\}$NMR spectrum of the of zirconium(IV) complexes are in agreement with ^{1}H NMR. The $^{13}C\{^1H\}$NMR spectrum of the $Zr(L^1)_2$ complex (Fig. 2) shows the two iminic carbon, C(7) and

C(14), resonances, as functional group signals at 161.3 and 159.6 ppm, respectively. According to the spectrum, $Zr(L^1)_2$ complex has 24 signals, showing that the structures in solution are indicative of the magnetically non-equivalence environment of these carbons but the $^{13}C\{^1H\}$NMR spectrum of the $Zr(L^{1\prime})_2$ complex (Fig. 4) has 11 signals, indicating that the structures in solution are indicative of the magnetically equivalence environment, therefore the ^1H and $^{13}C\{^1H\}$NMR, spectra of complexes in $CDCl_3$ revealed the coordination of the Schiff base ligands to zirconium obviously.

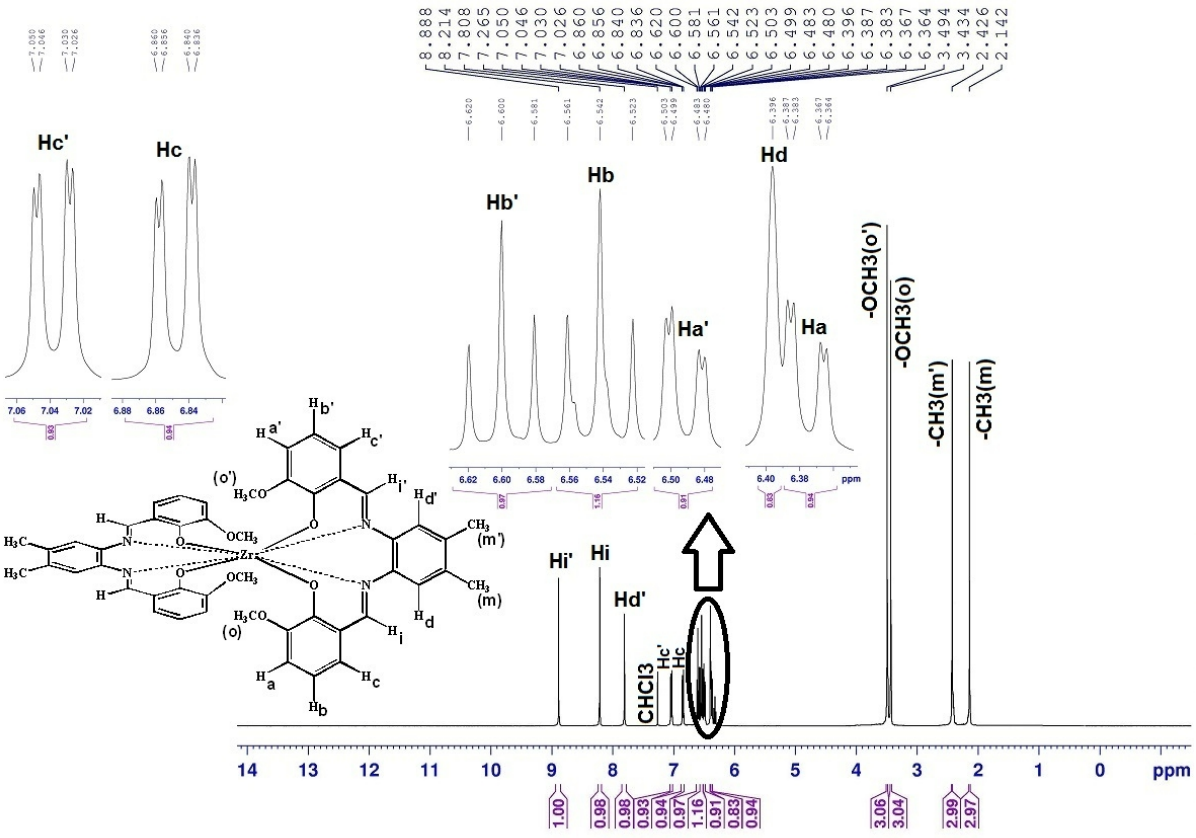


Fig. 1. ^1H NMR spectrum of $Zr(L^1)_2$ in $CDCl_3$.

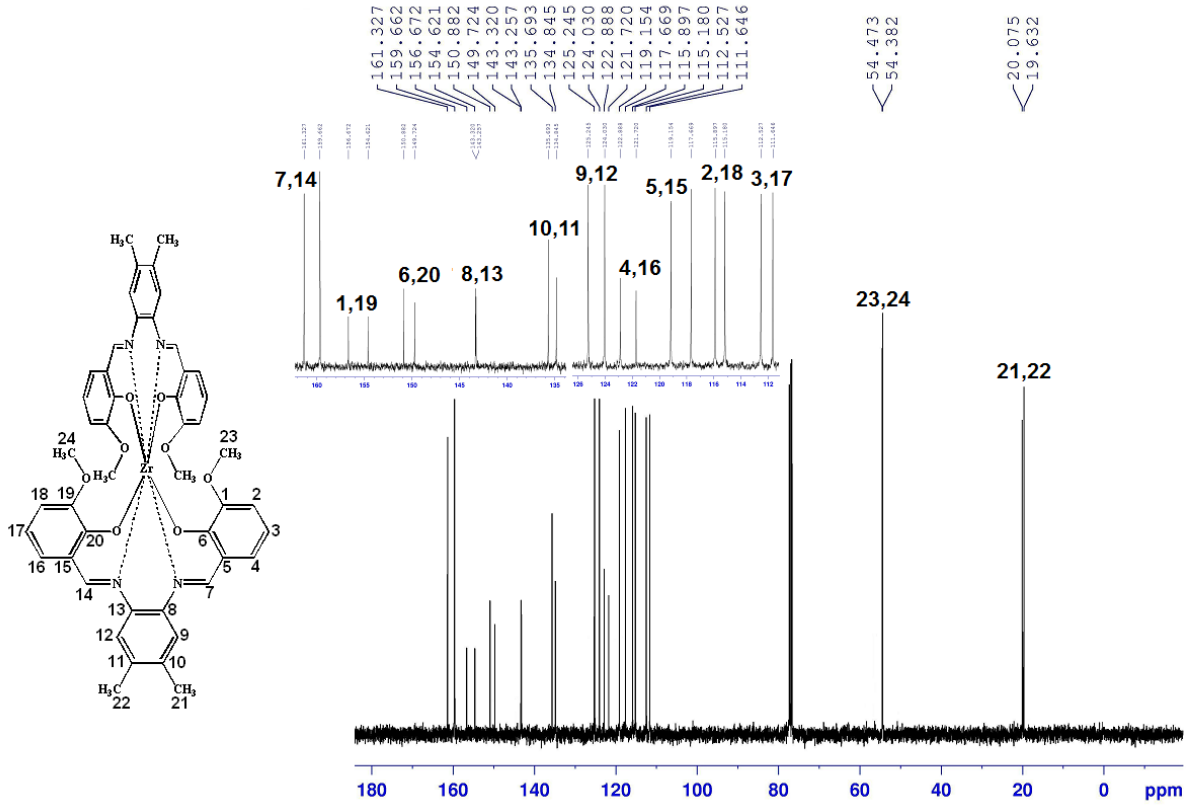


Fig. 2. $^{13}C\{^{1}H\}$NMR spectrum of $Zr(L^1)_2$ in $CDCl_3$.

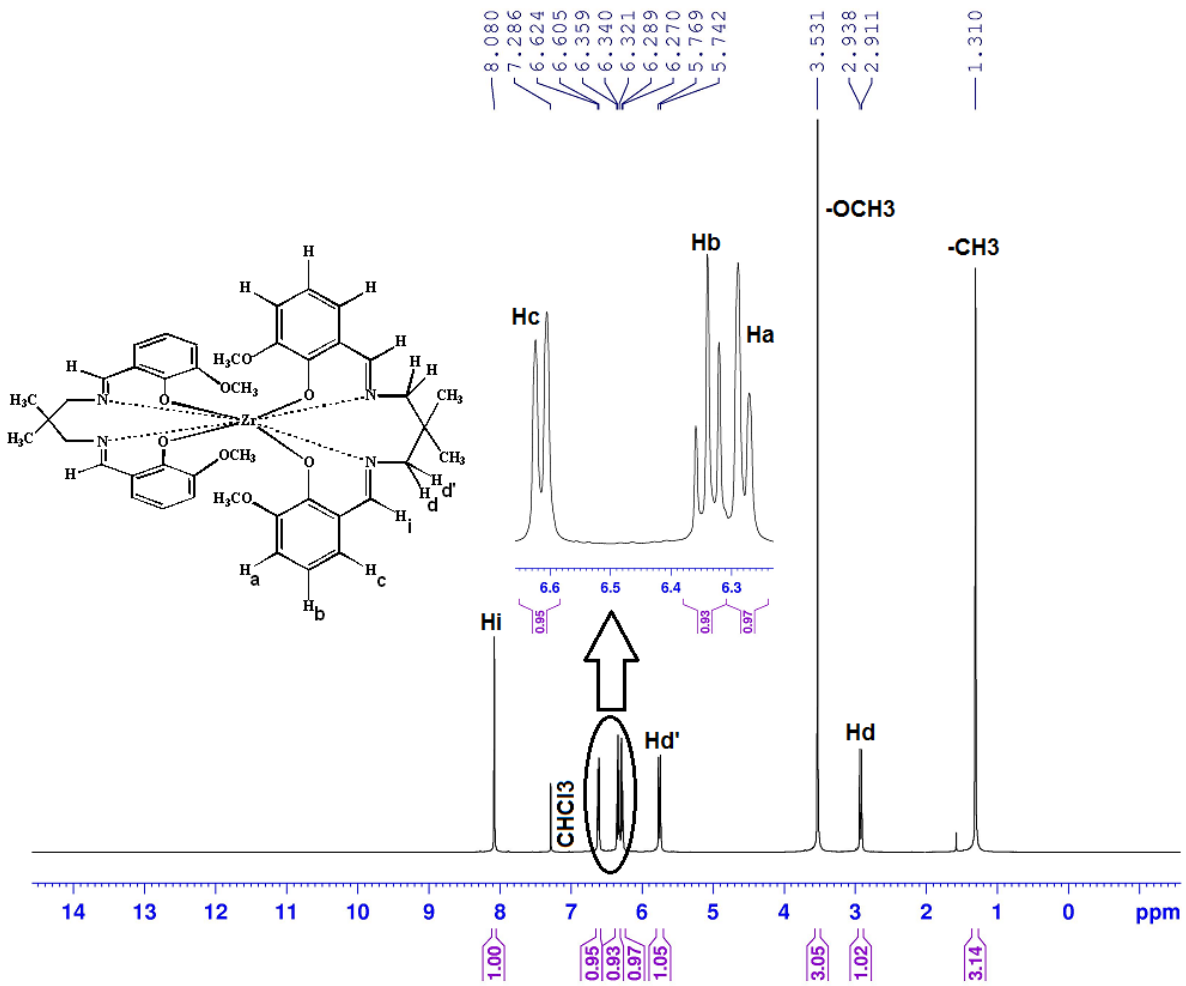


Fig. 3. ^{1}H NMR spectrum of $Zr(L^{1\prime})_2$ in $CDCl_3$.

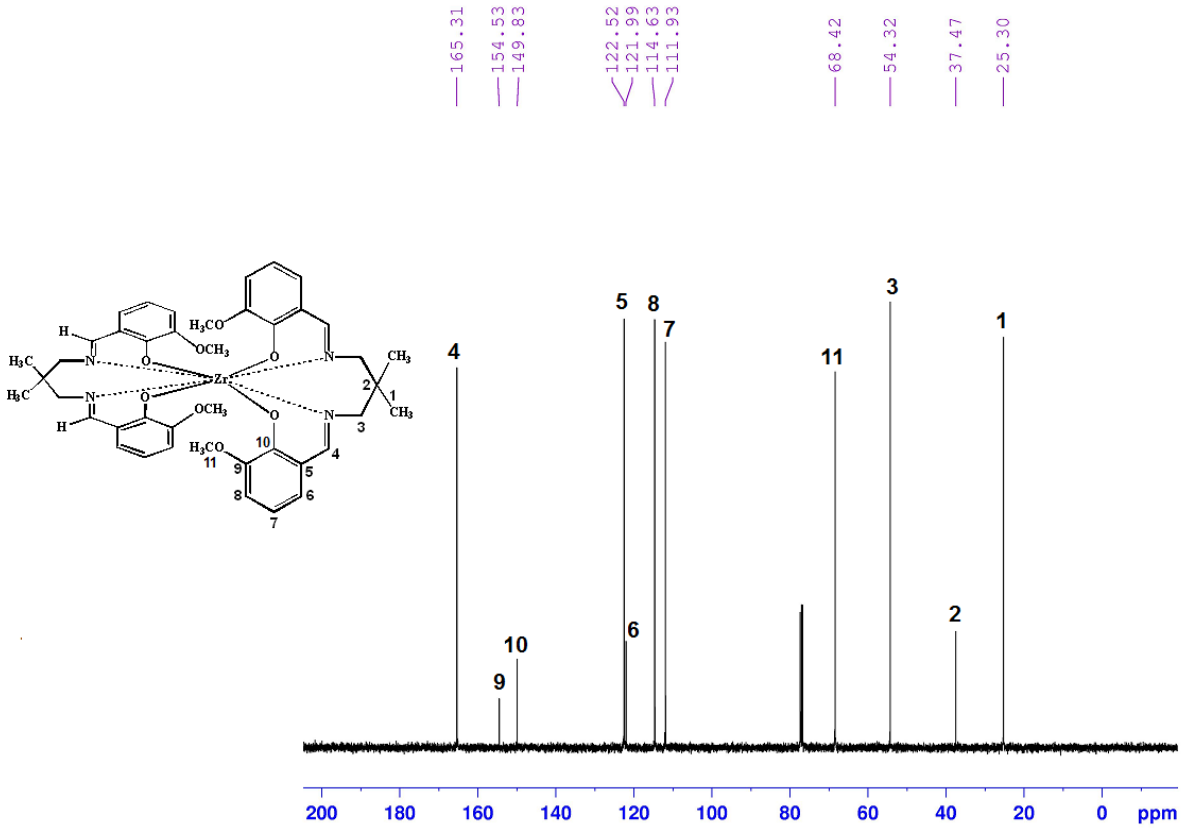


Fig. 4. $^{13}C\{^{1}H\}$NMR spectrum of $Zr(L^{1\prime})_2$ in $CDCl_3$.

X-Ray crystallography

The solid state structures of **$Zr(L^{1\prime})_2$**, **$Zr(L^{3\prime})_2$** and **$Zr(L^{3})_2$** complexes were studied by X-ray diffraction. The crystal data and refinement parameters of the complexes are summarized in Table 2. The ORTEP of **$Zr(L^{1\prime})_2$**, **$Zr(L^{3\prime})_2$** and **$Zr(L^{3})_2$** are shown in Fig. 5. Selected bond lengths and angles are summarized in Table 3. The coordination environment of the metal in all complexes is eight-coordinate occupied by N_2O_2 sets of the coordinated ligands in distorted square-antiprism geometry. In **$Zr(L^{1\prime})_2$** and **$Zr(L^{3\prime})_2$**, each ligand behaves in tetradentate mode in which N_2O_2 donor atoms of each ligand occupy top and bottom coordination sites of Zr in the square-antiprism. The angle of the least square planes of the coordinated ligands with N_2O_2 atoms in **$Zr(L^{1\prime})_2$** and **$Zr(L^{3\prime})_2$** is 89.23(9) and 89.81(6)°, respectively. The N_2O_2 cores on the top and bottom of the Zr center are close to planarity [maximum displacement -0.017(2), -0.054(2), -0.079(1), and -0.045(1)

Å for O1/O8/N1/N4, O4/O5/N2/N3 in **Zr(L$^{1\prime}$)$_2$**, and **Zr(L$^{3\prime}$)$_2$** respectively] and nearly parallel to each other [dihedral angle 0.37(16) and 0.25(14)° in the complexes, respectively]. The asymmetric unit of the **Zr(L^3)$_2$** complex comprises a mononuclear Zr complex with the tetradentate ligand H_2L^3. The N_2O_2 donor set of the symmetry related ligands occupy the corner of each square on the top and bottom of the Zr center giving rise to a square-antiprism arrangement of the donor atoms. The N_2O_2 cores on the top and bottom of the Zr center are close to planarity [maximum displacement 0.013(1) Å for O1/O2/N1/N2] and nearly parallel to each other with dihedral angle 1.53(1)°. The Zr–N and Zr–O bond lengths and geometry of the coordinated ligand around Zr in complex **Zr(L^3)$_2$** are comparable to the related Zr(salophen)$_2$ complex [13]. The Zr–N and Zr–O bond lengths in complex **Zr(L$^{1\prime}$)$_2$**, and **Zr(L$^{3\prime}$)$_2$** are comparable to the previously published structures [39]. The interesting feature of the crystal packing of **Zr(L$^{3\prime}$)$_2$** is the intermolecular C5–H5···O6 interaction forming one dimensional infinite chain of the complexes running along the *c*-axis (Fig. 6).

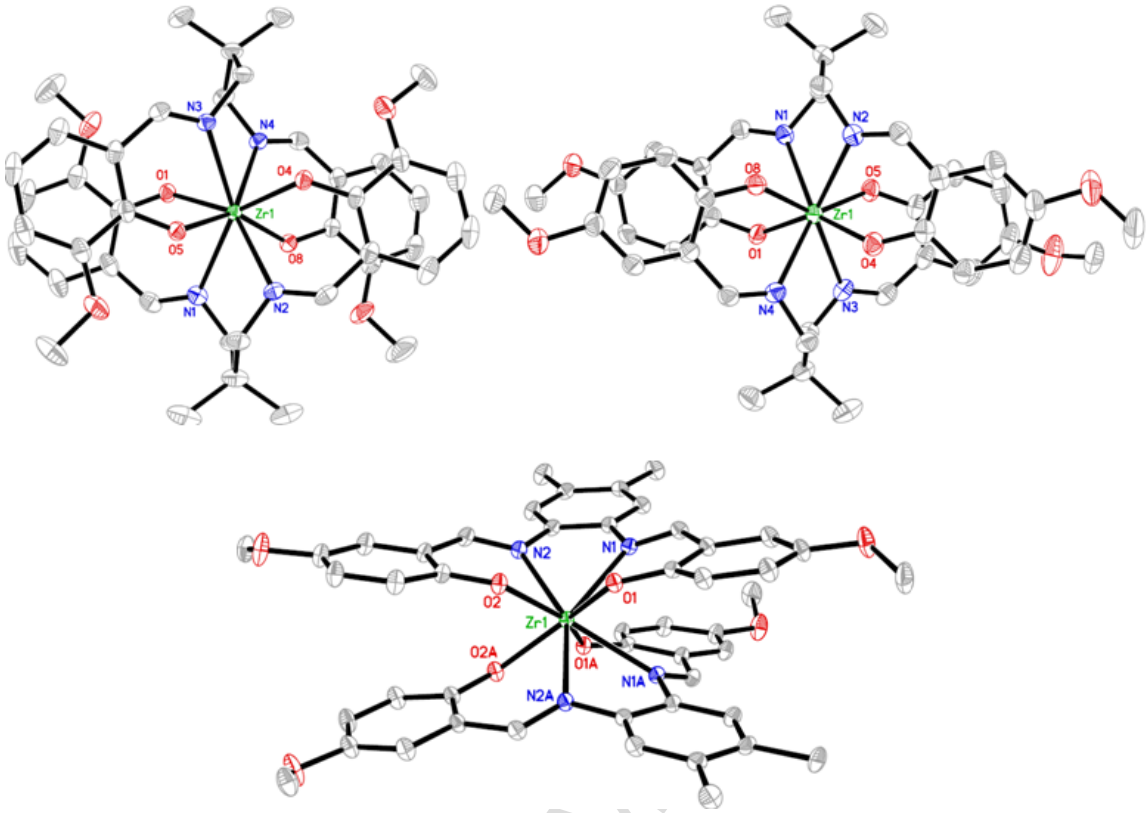


Figure 5. The ORTEP of $\mathbf{Zr(L^{1\prime})_2}$ (left), $\mathbf{Zr(L^{3\prime})_2}$ (right) and $\mathbf{Zr(L^{3})_2}$ (bottom) complexes. Hydrogen atoms were omitted for clarity.

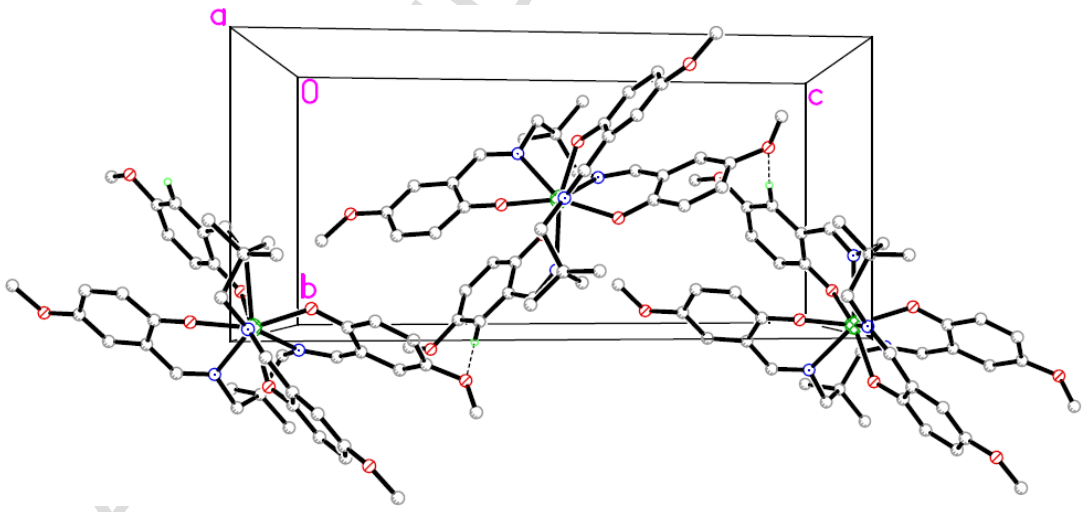


Figure 6. The packing of $\mathbf{Zr(L^{3\prime})_2}$ viewed down the *a*-axis showing one dimensional extended chain along *c*-axis.

Table 2. Crystal data and refinement parameters of **$Zr(L^{1\prime})_2$**, **$Zr(L^{3\prime})_2$** and **$Zr(L^3)_2$**

Complex	**$Zr(L^{1\prime})_2$**	**$Zr(L^{3\prime})_2$**	**$Zr(L^3)_2$**
Empirical formula	$C_{42}H_{48}N_4O_8Zr$	$C_{42}H_{48}N_4O_8Zr$	$C_{48}H_{44}N_4O_8Zr$
Formula mass	828.06	884.7	896.09
Crystal size (mm)	0.18 × 0.20 × 0.25	0.22 × 0.25 × 0.30	0.16 × 0.18 × 0.26
Colour	light-yellow	light-yellow	light-yellow
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1/c$	*Pbcn*
θ_{max} (°)	27.2	26.0	28.3
a (Å)	11.0403(6)	21.0777(18)	13.4549(8)
b (Å)	14.4722(8)	9.5534(6)	21.6826(13)
c (Å)	13.4025(9)	20.2209(17)	13.6122(7)
α (°)	90	90	90
β (°)	112.654(2)	99.900(3)	90
γ (°)	90	90	90
V (Å³)	1976.2(2)	4011.1(5)	3971.2(4)
Z	2	4	4
D_{calc} *(Mg/m³)*	1.392	1.371	1.499
μ (mm⁻¹)	0.336	0.331	0.341
F (000)	864	1728	1856
Index ranges	-14 ≤ h ≤ 11	-25 ≤ h ≤25	-17 ≤ h ≤17
	-17 ≤ k ≤ 18	-11 ≤ k ≤11	-28 ≤ k ≤26
	-17 ≤ l ≤ 17	-24 ≤ l ≤24	-17 ≤ l ≤16
No. of measured reflns.	17032	30679	34499
No. of independent reflns./R_{int}	8446/0.032	7889/0.038	4911/0.074
No. of observed reflns. I > 2σ(I)	7096	5517	2904
No. of parameters	504	504	280
Goodness-of-fit (GOF)	1.00	1.02	1.02
R_1 (observed data)	0.0388	0.0426	0.0406
wR_2 (all data)	0.0701	0.1167	0.1017

Table 3. Selected bond lengths (Å) and angles (°) of **$Zr(L^{1\prime})_2$**, **$Zr(L^{3\prime})_2$** and **$Zr(L^3)_2$**

Bond lengths (Å)	**$Zr(L^{1\prime})_2$**	**$Zr(L^{3\prime})_2$**	**Bond lengths (Å)**	**$Zr(L^3)_2$**
Zr(1)–O(1)	2.080(3)	2.071(2)	Zr(1)–O(1)	2.1044(16)
Zr(1)–O(4)	2.074(3)	2.057(2)	Zr(1)–O(2)	2.1136(18)
Zr(1)–O(5)	2.069(3)	2.070(2)	Zr(1)–N(1)	2.416(2)
Zr(1)–O(8)	2.079(3)	2.059(2)	Zr(1)–N(2)	2.385(2)
Zr(1)–N(1)	2.453(4)	2.484(3)		
Zr(1)–N(2)	2.459(4)	2.499(3)		
Zr(1)–N(3)	2.455(4)	2.475(3)		
Zr(1)–N(4)	2.455(3)	2.453(3)		
Bond angles (°)			**Bond angles (°)**	
O(1)–Zr(1)–O(4)	144.56(12)	143.62(9)	O(1)–Zr(1)–O(2)	75.25(7)
O(1)–Zr(1)–O(5)	84.58(11)	102.35(8)	O(1)–Zr(1)–N(1)	73.03(7)
O(1)–Zr(1)–O(8)	107.62(11)	88.53(8)	O(1)–Zr(1)–N(2)	113.00(7)
O(1)–Zr(1)–N(1)	73.41(14)	73.28(8)	O(2)–Zr(1)–N(1)	112.26(7)
O(1)–Zr(1)–N(2)	140.16(14)	142.67(9)	O(2)–Zr(1)–N(2)	74.22(7)
O(1)–Zr(1)–N(3)	77.67(13)	73.10(9)		
O(1)–Zr(1)–N(4)	72.93(12)	78.09(8)		
O(4)–Zr(1)–O(5)	105.14(12)	87.65(8)		
O(4)–Zr(1)–O(8)	84.21(11)	105.13(8)		

Antibacterial activity

The synthesized Schiff-base ligands H_2L^x, $H_2L^{x'}$ and their zirconium(IV) complexes $[Zr(L^x)_2]$, $[Zr(L^{x'})_2]$ (x=x′=1,2,3,4) were tested for their in vitro antibacterial. The minimum inhibitory concentrations of the investigated compounds are summarized in Table 4. A comparative study of the ligands and the complexes indicates that the Zr compounds exhibit more profound antibacterial activity than free ligands. Such increase activity of the metal complexes can be explained on the basis of Overtone's concept [40] and Tweedy's chelation theory [41]. There is a decrease in the polarity of the Zr atom significantly after chelation, because of the partial sharing of its positive charge with the donor groups and also due to π-electron delocalization on the whole chelate ring. The Zr complexes interaction is preferred with the lipids and polysaccharides which are the important constituents of the cell wall and membranes. Furthermore, decreasing of polarity led to increasing the lipophilic character of the chelates and an interaction between the Zr complexes and the lipid is favoured which may lead to the subsequent breakdown of the permeability barrier of the cell resulting in obstruction with the normal cell processes [42]. Due to liposolubility, this is an important factor that controls antimicrobial activity.

The results revealed that the complexes $[Zr(L^x)_2]$ are the most effective against *Escherichia coli* and *Staphylococcus aureus* with MIC quantity of (2-4 μg/cm^3), while the complexes $[Zr(L^{x'})_2]$ are less effective (4-8 μg/cm^3) and relative ligands almost have no effectiveness. Because $[Zr(L^x)_2]$ complexes have less polarity than $[Zr(L^{x'})_2]$ complexes are due to the aromatic ring in the lipophilic diamine so more antibacterial activity.

Apparently, the Zr complexes are more toxic towards Gram-negative strain (*Escherichia coli*) than Gram-positive strain (*Staphylococcus aureus*). The reason probably lies in the difference between the structures of the cell walls, due to the peptidoglycan layer thickness (the middle layer of the

bacterial cell membrane) that is thinner in gram-negative bacteria than gram positive and the complex easier pass this layer.

Compared antibacterial properties of synthesized zirconium complexes with other similar complexes show that these complexes are more active and the structural features of these complexes may contribute to the activity of these complexes [43, 44].

Table 4 The inhibition diameter zone values (mm), MIC and MBC of the ligands and their corresponding Zr(IV) complexes

compound	MIC (mg/ml)		MBC (mg/ml)		Inhibition zone (mm)	
	E. coli	*S. aureus*	*E. coli*	*S. aureus*	*E. coli*	*S. aureus*
H_2L^1	0.128	0.128	0.128	0.128	8	7
$Zr(L^1)_2$	0.002	0.004	0.002	0.008	13	11.7
H_2L^2	0.128	0.128	0.128	0.128	7	6.5
$Zr(L^2)_2$	0.002	0.004	0.002	0.008	14	12
H_2L^3	0.128	0.064	0.128	0.064	8	8
$Zr(L^3)_2$	0.001	0.002	0.001	0.004	15	13.3
H_2L^4	0.128	0.128	0.128	0.128	8.3	7
$Zr(L^4)_2$	0.002	0.004	0.002	0.008	13.7	11.6
$H_2L^{1'}$	0.128	0.128	0.128	0.128	_	_
$Zr(L^{1'})_2$	0.004	0.008	0.008	0.016	11.2	10.5
$H_2L^{2'}$	0.128	0.128	0.128	0.128	_	_
$Zr(L^{2'})_2$	0.004	0.008	0.008	0.016	11.5	10.7
$H_2L^{3'}$	0.128	0.128	0.128	0.128	_	_
$Zr(L^{3'})_2$	0.002	0.004	0.004	0.008	12.7	11
$H_2L^{4'}$	0.128	0.128	0.128	0.128	_	_
$Zr(L^{4'})_2$	0.004	0.008	0.008	0.016	11.3	10

Conclusions

We have reported the synthesis of new zirconium(IV) Schiff-base complexes of two potentially tetradentate ligands. The ligands and their respected zirconium(IV) complexes were characterized by spectroscopic techniques and elemental analyses (CHN). The single crystal X-ray diffraction analysis of the complexes revealed that the coordination environment of the metal in all complexes is eight-coordinate occupied by N_2O_2 sets of the coordinated ligands in distorted square-antiprism geometry. The biological activity of the compounds showed the zirconium(IV) complexes exhibit antimicrobial activity.

Appendix A. Supplementary data

CCDC **1526749-1526751** contain the supplementary crystallographic data for the **5**, **7** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- ► Synthesis, characterization and spectral properties of new Zr(IV) Schiff base complexes.
- ► Selective geometry around Zr(IV) by tuning the steric hindrance of the coordinated ligands.
- ► Structural and biological studies of the new Zr(IV) complexes.